

Synthesis and Properties of Methano-bridged Tetradehydro-[20]-, -[24]-, -[26]-, -[28]-, -[30]- and -[32]-annulenediones

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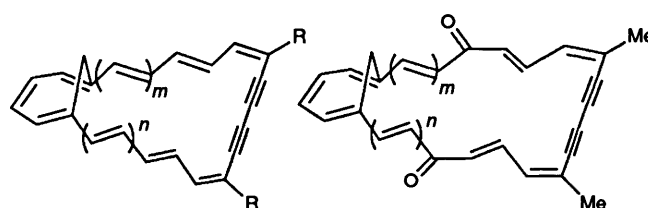
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The title annulenediones **4–9** have been synthesized by first an aldol condensation of cyclohepta-1,3,5-triene-1,6-dicarbaldehyde **10** or its vinylogous dialdehydes **11–14** with acetone to afford the dimethyl diketones **16–20** and then by a second aldol condensation of 1,6-diacetylcyclohepta-1,3,5-triene **15** or the dimethyl diketones **16–20** with (*Z*)-3-methylpent-2-en-4-ynal **21**, followed by intramolecular oxidative coupling of the resulting acyclic diacetylenes. The properties of the title compounds are discussed on the basis of ¹H NMR and electronic spectra as well as cyclic voltammetry.

In previous papers, we have confirmed the alternation of the tropic nature between $[4n + 2]\pi$ - and $[4n]\pi$ -electron systems in dimethyl- or trimethyl-tetradehydroannulenediones **1** with 13- to 25-membered rings.^{1,2} On the other hand, although several annulenediones with an additional carbonyl group are known, there are few with a 20–30-membered ring size.³ Judging from the fact that annulenediones showed a much smaller degree of dia- or para-tropicity than did the corresponding carbocyclic annulenes,⁴ annulenediones were expected to show even smaller tropicity than do annulenediones. However, the dimethyl-hexadehydro[16]annulenedione **2** prepared by Lombardo and Sondheimer proved to be clearly diatropic, indicating the significant contribution of the canonical form **2a**, and showed even stronger diatropicity in D₂SO₄, suggesting the formation of the dication **2b**.⁵

Recently, we reported that the tetradehydromethanoannulenes **3** show diatropism up to the 34-membered ring (**3**; $m = n = 4$) in $[4n + 2]\pi$ -electron series and paratropism up to the 28-membered ring (**3**; $m = 3, n = 2$) in the $[4n]\pi$ -electron series, respectively, and that these compounds have high thermal and conformational stability, which is reasonably ascribed to the considerable rigidity of the molecular skeleton imposed by the presence of the bridging methylene group and a 1,3-diacetylenic linkage.^{6,7}

This and the availability of a series of vinylogues of cycloheptatriene-1,6-dicarbaldehyde,^{6–8} in connection with the search for two-dimensional, π -electron-conjugated compounds with nonlinear optical behaviour,⁹ prompted us to prepare the methano-bridged annulenediones.¹⁰ Since a methano-bridge should contribute to keeping the annulenedione perimeter rigid,^{6–8} it was expected that the title annulenediones would show the ring-current effect for the $[4n + 2]\pi$ - or $[4n]\pi$ -electron system arising from polarization of two carbonyl groups, and their dideuteriated species would show the much greater ring-current effect that compound **2** and its dideuteriated species **2b** showed, as mentioned above. Contrary to



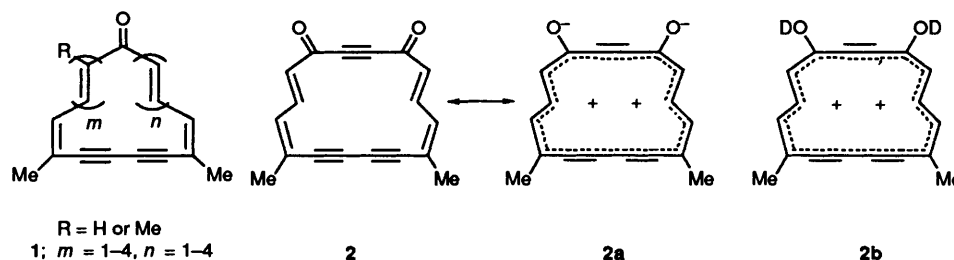
R = Me or Bu'
3; $m = 1–5, n = 1–5$

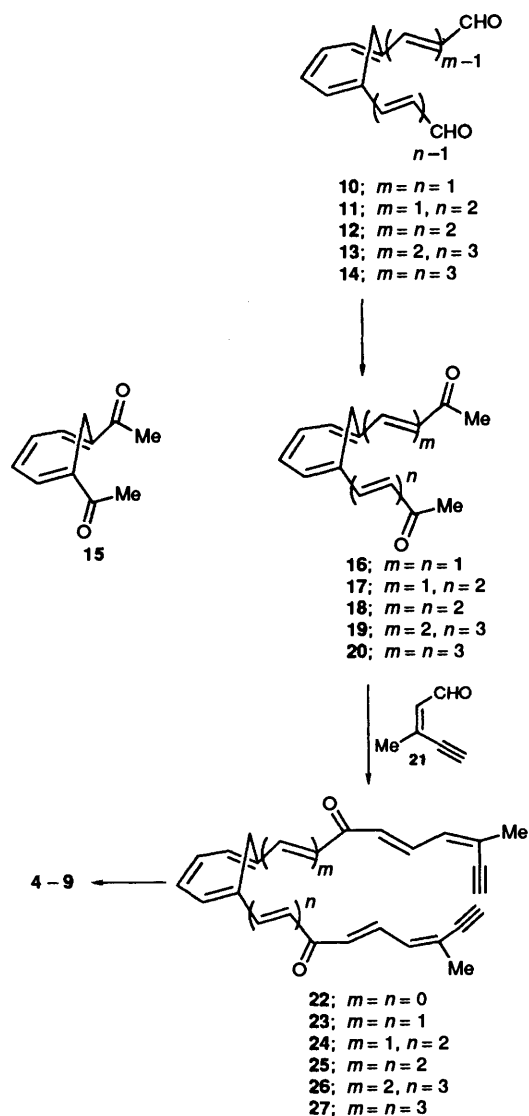
[20]-**4**; $m = n = 0$
 [24]-**5**; $m = n = 1$
 [26]-**6**; $m = 1, n = 2$
 [28]-**7**; $m = n = 2$
 [30]-**8**; $m = 2, n = 3$
 [32]-**9**; $m = n = 3$

this expectation, however, the annulenediones **4–9** prepared in this study showed at most only weak tropicity or none at all, presumably due to low planarity of their molecular skeletons. The dideuteriated species **5B** formed from the tetradehydromethano[24]annulenedione **5** proved to be strongly diatropic; this is the largest dideuteriated annulenedione species to show the ring-current effect so far.³

Results and Discussion

Synthesis.—The tetradehydromethanoannulenediones **4–9** were synthesized according to the reaction sequence illustrated in Scheme 1. The starting materials were the dicarbaldehydes **10–14** and 1,6-diacetylcyclohepta-1,3,5-triene **15**. Compound **15** was the intermediate for the synthesis of the dicarbaldehyde **10** and was prepared as reported.¹¹ Successive homologations of the dicarbaldehyde **10** to the vinylogous dicarbaldehydes **11–14** were carried out according to the previously reported method.^{6–8} The aldol condensations of the dicarbaldehydes **10–14** with acetone in the presence of aqueous alkali afforded the corresponding dimethyldiketones **16–20** in 69–76% yield.





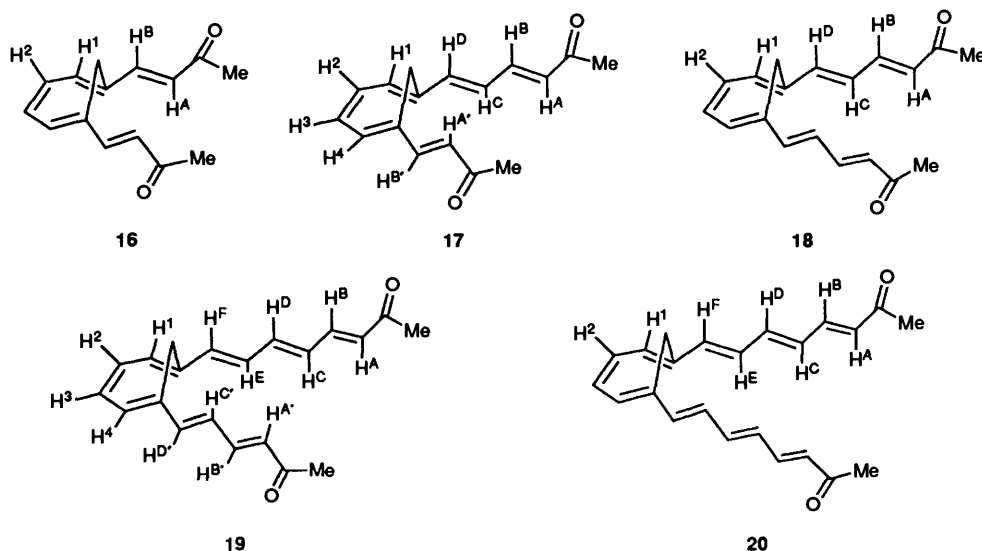
Scheme 1

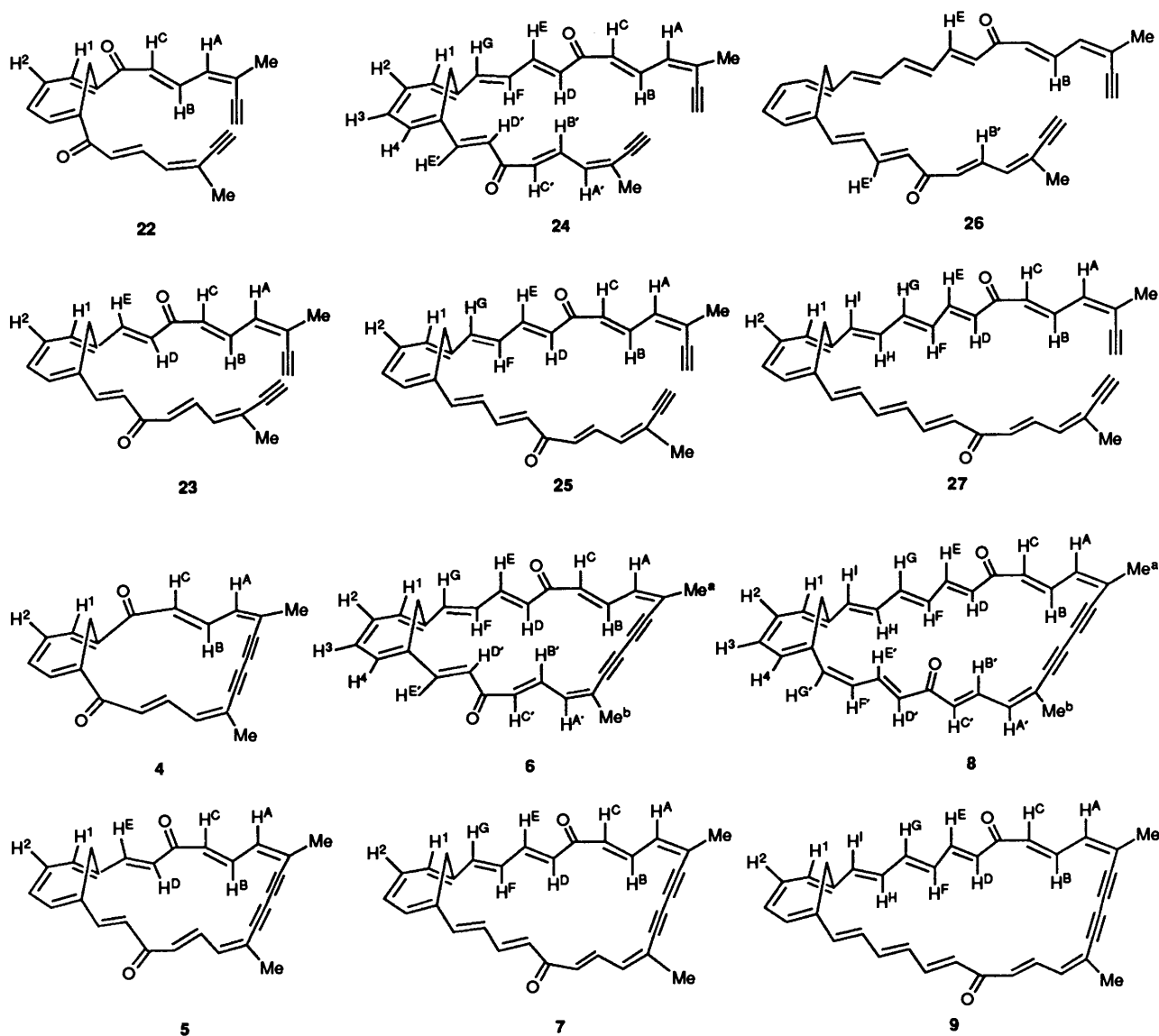
Attempted condensation of the diketone **16** with (*Z*)-3-methylpent-2-en-4-ynal **21**^{1a,12} in the presence of dilute ethanolic sodium ethoxide in diethyl ether or benzene was without success. After several unsuccessful experiments, it was found that the aldol condensations of 1,6-diacetyl-

cyclohepta-1,3,5-triene **15** and the dimethyldiketones **16–20** with the aldehyde **21** in the presence of concentrated ethanolic sodium ethoxide in benzene proceeded successfully, affording the corresponding acyclic diketones **22–27** in 41–85% yield. Intramolecular oxidative couplings of the acyclic compounds **22–27** were carried out either with anhydrous copper(II) acetate in pyridine–diethyl ether under relatively dilute conditions^{1a,13} or with copper(II) acetate monohydrate in pyridine–methanol under high-dilution conditions with diethyl ether as an entraining solvent,¹² giving rise to the monomeric cyclic compounds **4–9** in 32–61% yield. It is noteworthy that the intramolecular oxidative couplings in the preparation of compounds **4–9** proceeded in more satisfactory yields than in the case of the preparation of the tetrahydromethanoannulenes **3**,^{6,7} presumably because of the higher thermal stability of compounds **22–27** than the corresponding acyclic precursors of compounds **3**. Tetrahydromethano-[20]-annulenedione **4**, -[24]annulenedione **5**, -[26]annulenedione **6**, -[28]annulenedione **7**, -[30]annulenedione **8**, and -[32]annulenedione **9**, so obtained, formed thermally relatively stable, yellow, orange, red, or purple crystals.

Structures of these annulenediones are discussed in the next section. Both the first and the second aldol condensation always gave the products with *E*-configuration for the newly formed double bonds, as shown in their structural formula. However, in the formation of the tetrahydromethano-[30]annulenedione **8**, configurational isomerization of a double bond occurred during the intramolecular oxidative coupling (see below). A similar change has been observed in the preparation of methanothia[19]- and -[23]-annulene,⁸ tetrahydro[15]annulene¹⁴ and tetrahydrotribenzo[14]-annulene.¹⁵

¹H NMR Spectra and Geometrical Determination.—Chemical-shift assignments for the olefinic protons in the annulenediones **4–9** and their precursors **22–27** were made as follows. Broad doublet signals were assigned to the terminal protons of the polyenone chain adjacent to a methyl group, because the broadening was due to allylic coupling to the methyl protons as revealed by decoupling experiments, while sharp doublets were assigned to the protons adjacent to a carbonyl group or the cycloheptatriene ring. Then the proton sequence along the polyene moiety was determined by successive decoupling experiments. When an ambiguous assignment was left, the spectral data were compared with the closely related, lower homologue; for example between compounds **23** and **25**, and between compounds **7** and **9**.





Molecular geometries were deduced as follows. Irradiation of the methyl signals not only sharpened the doublet signals due to the respective adjacent olefinic protons H^A (and H^A') but also enhanced the intensity of these signals due to the nuclear Overhauser effect (NOE), clearly indicating that H^A (and H^A') is located outside the macrocyclic ring. The relative arrangement of the olefinic proton was deduced from vicinal coupling constants; 14–16 Hz for an *E* double bond, 9–11 Hz for a *Z* double bond, 10–12 Hz for an *s-trans* single bond between two double bonds, and 5–7 Hz for an *s-cis* single bond.¹⁶ Thus the molecular geometries shown by the structural formula were concluded.

The NOESY spectrum was obtained for compound **6**, which confirmed both the chemical shift and geometry assignments for this compound as mentioned above.

It is interesting to note that only compound **8** among the annulenediones **4–9** has a *Z*-CH=CH bond despite the 'all-*E*' configuration of the precursor **26**. Although the exact reason for this remains to be clarified, this geometry can be thermodynamically more stable than the 'all-*E*' one.

The methylene protons in compound **4** give an extremely broad signal in $CDCl_3$ at 26 °C, while those in the other annulenediones **5–9** give a sharp singlet reflecting rapid flipping of the methylene moiety. The details of the dynamic behaviour are discussed in a later section.

The 1H NMR chemical shift data of the annulenediones **4–9** and the acyclic precursors **22–27** are listed in Table 1 and the 1H NMR spectra of the tetradehydro[24]annulenedione **5** taken in $CDCl_3$, CF_3CO_2D and D_2SO_4 at room temperature are shown in Fig. 1.

Since the hexadehydro[16]annulenedione **2** showed diatropicity as a 14π -electron system arising from polarization of the two carbonyl groups,⁵ the tetradehydro[20]annulenedione **4** was also expected to show diatropicity as an 18π -electron system due to polarization. However, comparison of the proton chemical shifts of the [20]annulenedione **4** with those of the corresponding acyclic model compound **22** (Table 1) indicates that the annulenedione **4** is atropic, since the downfield shift of the outer protons (including methyl protons) is not seen although the inner protons H^B shift upfield.

If both of the carbonyl groups of compound **4** are protonated to form a dicationic species, compound **4** would be expected to show diatropicity. Therefore, 1H NMR spectra of compound **4** were taken in acidic media and the data are also given in Table 1. In deuteriotrifluoroacetic acid (CF_3CO_2D), all the olefinic protons show a downfield shift by 0.16–0.42 ppm from those in deuteriochloroform ($CDCl_3$), which indicates that compound **4** exists probably as a rapidly equilibrating, monodeuteriated species ($4A \rightleftharpoons 4A'$) and that contribution of a dication $4B$ is very low, if any. Upon changing the medium from CF_3CO_2D to

Table 1 ^1H NMR parameters of the compounds **22–27** and **4–9** at 26 °C^a

Compound	δ_{H} Inner protons		Outer protons						
	H ^B	H ^D	CH ₂	H ^A	H ^C	H ^E	H ¹	H ²	Me
22 ^b	7.78		3.08	6.51	6.95		6.94	7.26	2.03
4	7.14		<i>c</i>	6.59	6.21		7.00	6.89	1.93
4A ^d	7.56		2.22, 4.18 ^e	6.76	6.45		7.13	7.30	2.03
4B ^f	6.94		2.38, 3.89	7.12	6.68		7.14	7.28	2.12
23	7.75	6.70	2.78	6.48	6.49	7.41	6.66	6.80	2.05
5	7.22	6.65	2.80	6.61	6.55	7.53	6.68	6.68	2.11
5A ^d	7.22–7.12	6.30	2.50	7.22–7.12	6.97	8.27	7.22–7.12	7.23	2.39
5B ^f	5.1	3.93	0.53	7.46	6.91	8.86	7.19	7.61	2.29
24 ^g			2.78						2.05
6 ^g			3.04						2.07, 2.05
25 ^g			2.77						2.04
7 ^g			2.74						2.16
26 ^g			2.76						2.04
8 ^g			2.94						2.07, 2.05
27 ^g			2.74						2.04
9 ^g			2.66						2.18

^a Obtained in CDCl_3 at 500 MHz unless otherwise stated. ^b Taken at 90 MHz. ^c Too broad to be detected. Observed as an AB quartet at -36 °C; δ 1.93 and 4.18 (J 13.6 Hz). ^d In $\text{CF}_3\text{CO}_2\text{D}$. ^e Broad signals observed as an AB quartet at -26 °C; δ 2.28 and 4.19 (J 14.0 Hz). ^f In D_2SO_4 . ^g Data for the olefinic protons are omitted (see Experimental section).

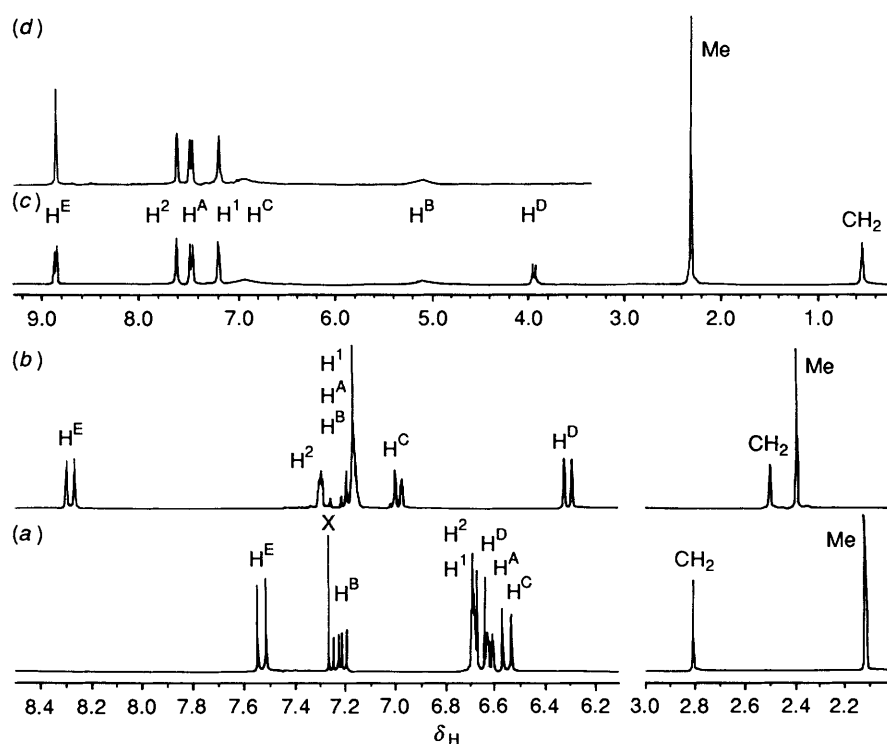
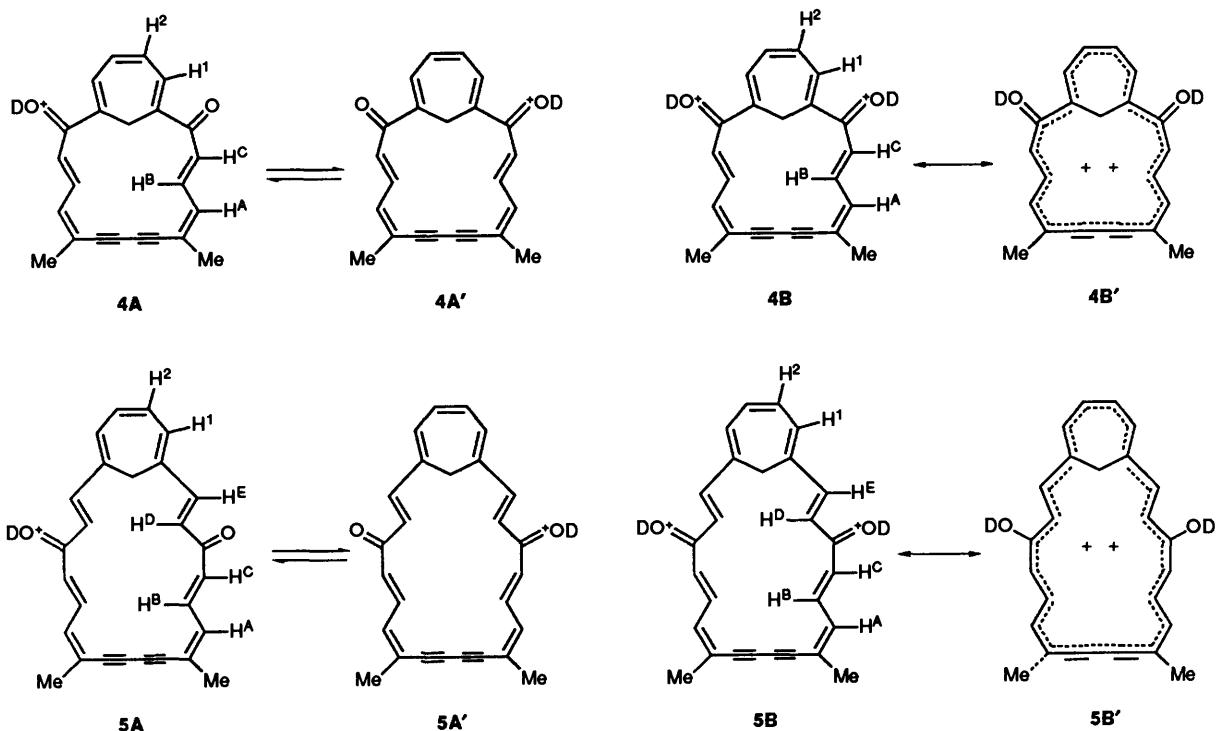


Fig. 1 500 MHz ^1H NMR spectra of compound **5** at 26 °C: (a) in CDCl_3 ; (b) in $\text{CF}_3\text{CO}_2\text{D}$; (c) in D_2SO_4 measured immediately after dissolution; and (d) in D_2SO_4 measured 2 days later. In (a) and (b), the intensities of the Me and CH_2 are reduced. The peak labelled X is due to CHCl_3 .

D_2SO_4 , the protons H^{A} and H^{C} move further downfield but the proton H^{B} moves upfield by 0.62 ppm, which might be explainable in terms of the ring-current effect. Although the inner proton H^{B} resonates at a lower field than the outer proton H^{C} , this anomaly may be ascribed to the deshielding anisotropy effect of the diyne moiety on H^{B} , as observed in the related [1,3]cyclophanepolyenediynes compounds.⁶ The fact that compound **4** is diatropic in D_2SO_4 suggests that compound **4** exists in this medium mainly as a dicationic species **4B'** where the delocalized 18π -electron structure **4B'** contributes to some extent, although the magnitude is very low, compared with that in the case of the hexadehydro[16]-**2**⁵ and the tetrahydro[24]annulenedione **5** in D_2SO_4 (see below) because of the low planarity of the species **4B** as suggested by inspection of the molecular model.

On the other hand, the tetrahydro[24]annulenedione **5** might be at most weakly diatropic in CDCl_3 , as expected of a 22π -electron system, since most of the outer protons (including the methyl protons) in compound **5** resonate at a lower field than the corresponding protons in the acyclic model compound **23**, whereas the inner protons resonate at a higher field, although the methylene protons do not show the upfield shift (Table 1). However, even if the anisotropic effect of the diacetylene moiety is taken into account, the fact that H^{B} proton resonates at a lower field than the outer H^{A} and H^{C} protons, as is seen from Fig. 1a, suggests that the [24]-annulenedione **5** is weakly diatropic, if at all.

Although the annulenedione **5** is weakly diatropic under neutral conditions (CDCl_3), it is clearly diatropic in acidic media, as is seen from Table 1 and Fig. 1. In $\text{CF}_3\text{CO}_2\text{D}$ the



outer olefinic protons (H^A , H^C , H^E , H^1 and H^2) as well as the methyl protons resonate at a lower field than in $CDCl_3$, whereas the inner H^B , H^D and the methylene protons move upfield, suggesting the formation of the diatropic monodeuterated species, which are in rapid equilibrium between **5A** and **5A'**, as was compound **4** in CF_3CO_2D (**4A** \rightleftharpoons **4A'**).

Upon changing the medium from CF_3CO_2D to D_2SO_4 , the inner H^D and the methylene protons move significantly upfield while the outer H^A and H^E protons shift downfield, indicating the formation of the highly diatropic dideuterated species **5B** where the delocalized 22π -electron structure **5B'** contributes to a great extent.

Two interesting features are noted in the 1H NMR spectrum of compound **5** in D_2SO_4 . One is that the signals assigned to H^B and H^C are quite broad (Figs. 1c and 1d). This is ascribed to rapid flipping of the $CH^B=CH^C$ moiety around the adjacent single bonds. Upon lowering of the temperature from $26^\circ C$ to *ca.* $0^\circ C$, the H^B signal moves further upfield, while H^C moves downfield, by ~ 0.3 ppm, although no sharpening of the signals is observed. Thus the geometry shown by the formula **5B** represents the predominant conformer, and a small amount of other conformers are in rapid equilibrium with this one. The presence of other conformers in D_2SO_4 and their absence in $CDCl_3$ may be due to subtle differences in molecular strain between the neutral and deuterated species depending on the medium.

The other feature is the occurrence of H/D exchange of H^D in this medium. The doublet signal at δ 3.93 due to H^D is smaller than the normal two-proton intensity even immediately after preparation of the sample solution (Fig. 1c) because of the H/D exchange and the signal at δ 8.86 due to H^E appears as a mixture of a doublet and a singlet. The H^D signal is completely absent and the H^E signal is a sharp singlet two days later (Fig. 1d). The H/D exchange may occur by way of a tricationic species but it is not clear why H^D is selectively exchanged.

The simplest test for the nature of the ring currents in the annulenediones **6–9** is provided by the chemical shifts of the methylene and methyl protons, since these must always be inner and outer, respectively, and can readily be recognized. As is seen from Table 1, in the potentially $[4n]\pi$ -electron compounds **6**

and **8**, the inner methylene protons appear at lower field than those in the corresponding acyclic counterparts **24** and **26**, respectively, although no clear shift is observed for the methyl protons. On the other hand, in the potentially $[4n + 2]\pi$ -electron compounds **7** and **9**, the methyl protons show definite downfield shifts relative to those in the corresponding acyclic compounds **25** and **27**, while only a slight upfield shift is observed for the methylene protons. These observations suggest the paratropicity of the former and the diatropicity of the latter. However, as the magnitude of the extent of the alternation is quite small as compared with those observed in the series of tetrahydroannulenediones **1**^{1,2} and the tetrahydromethanoannulenediones **3**,^{6,7} the conclusion that the annulenediones **6–9** show at most weakly tropic nature might be exaggerated.

Attempts to obtain the corresponding dideuterated species from the annulenediones **6–9** were unsuccessful due to rapid decomposition of the diones **6–9** in D_2SO_4 solution.

Therefore, in rather surprising contrast to the cases of the hexadehydro[16]annulenedione **2**⁵ and the tetrahydromethanoannulenediones **3**,^{6,7} which exhibit a strong ring-current effect, the title annulenediones **4–9** were found to be only weakly diatropic or to be atropic. This indicates that compounds **3** have a more highly delocalized π -electron system than do compounds **4–9**. Inspection of molecular models reveals that the molecular skeletons of compounds **4–9** usually experience more severe steric strain than do those of compounds **3**, resulting in lower planarity of the molecular skeletons of **4–9** than those of compounds **3**. The polyene chain of compounds **3** has the odd number of carbon atoms between the cycloheptatriene ring and the diacetylene moiety, whereas the polyenone chain of compounds **4–9** has an additional carbon atom, *i.e.*, the even number of carbon atoms which may give the molecular skeletons more steric strain and thus reduce their planarity.

Flipping of the Methylene Bridge in Compound 4.—The methylene proton signal of the [20]annulenedione **4** showed a diverse appearance depending on the medium. In $CDCl_3$ at $26^\circ C$, the methylene signal was hardly detectable because it was extremely broad and buried under the baseline. At $-38^\circ C$

Table 2 Kinetic parameters for the methylene flipping in compound 4

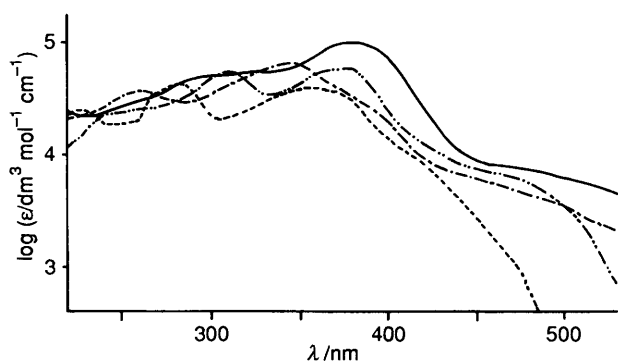
Solvent	ΔH^\ddagger / kcal mol ⁻¹ ^b	ΔS^\ddagger / cal mol ⁻¹ K ⁻¹ ^b	$k_{26^\circ\text{C}}$ / s ⁻¹	$\Delta G^\ddagger_{26^\circ\text{C}}$ / kcal mol ⁻¹ ^b	Method ^a
CDCl ₃	14.6 ± 0.3	4.7 ± 1.0	1400	13.2	TLA
CF ₃ CO ₂ D	15.4 ± 0.7	3.2 ± 2.3	170	14.5	TLA
D ₂ SO ₄			3.3	10.0	ST

^a TLA: total lineshape analysis; ST: saturation transfer. ^b 1 cal = 4.184 J.

Table 3 Electronic absorption maxima of the compounds 4–9 [a, in THF, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$); b, in H₂SO₄, λ_{max} (relative extinction coefficients)]. Strongest absorption indicated in bold type

4	a	230 (27 000), 271 (39 100) , 320 (18 300), 407sh (5 700)
	b	308 (0.75), 416 (1.00), 535 (0.33)
5	a	267sh (33 300), 283 (42 600) , 355 (39 200), 418sh (8 750)
	b	456sh (0.50), 485 (1.00), 614 (0.11)
6	a	264 (34 600), 344 (61 100) , 390sh (22 000)
	b ^a	345 (0.65), 400sh (0.94), 423 (1.00), 461sh (0.81), 627sh (0.32)
7	a	311 (52 600), 368sh (55 700), 380 (59 100) , 464sh (7 100)
	b ^a	438sh (0.83), 469 (1.00), 509 (0.83), 641 (0.22)
8	a	296 (46 700), 324sh (51 400), 381 (98 000)
	b ^a	474sh (0.93), 499 (1.00), 658sh (0.06)
9	a	280 (33 700), 338 (85 600), 389 (86 200) , 485sh (13 300)
	b	484sh (0.80), 515 (1.00), 559sh (0.46), 686sh (0.14)

^a These spectra changed with time.

**Fig. 2** Electronic absorption spectra of [24]- 5 (-----), [26]- 6 (--- · ---), [28]- 7 (.....) and [30]annulenedione 8 (——) in THF

it appeared as an AB quartet at δ 1.93 and 4.18 with J 13.7 Hz and at 60 °C a broad singlet was observed at δ 3.08. This suggests that the molecule adopts a conformation in which the methylene group is located out of the average plane of the macrocycle and the methylene protons are diastereotopic, although the precise geometry of the conformer is not known, and the interconversion between this and its mirror-image conformer by flipping of the methylene bridge through the average macrocyclic plane is taking place on the NMR time-scale. Total lineshape analysis of the signal in the temperature range 0–60 °C using the DNMR3 program¹⁷ afforded the kinetic parameters for the methylene flipping as shown in Table 2. In CF₃CO₂D the flipping was somewhat slower and the methylene protons gave two broad signals at 26 °C. The kinetic parameters were again obtained by total lineshape analysis at 26–70 °C as given in Table 2. In D₂SO₄ the methylene signal appeared as a definite AB quartet at 26 °C but irradiation of either one of the doublets caused a decrease in the intensity of the other together with decoupling. Quantitative saturation transfer experiments¹⁸ were carried out to give the rate constant for the flipping of 3.3 s⁻¹ at 26 °C (Table 2).

The energy barrier to the methylene flipping significantly increases by changing the solvent from CDCl₃ to CF₃CO₂D to D₂SO₄, suggesting that the rigidity of the macrocyclic ring increases in this order presumably owing to the decrease in

bond alternation. This result also supports the aforementioned inference that the charges are considerably delocalized to form an 18 π -electron system in D₂SO₄.

In any of the other annulenediones 5–9, the methylene protons give a sharp singlet in CDCl₃ at 26 °C, indicating the very fast flipping of the methylene moiety, although variable-temperature studies to obtain the kinetic parameters of flipping were not performed. The methylene proton signal of compound 5 at 26 °C becomes broader on changing the solvent from CDCl₃ to CF₃CO₂D to D₂SO₄, as shown by the relative heights of the methylene and methyl signals in Fig. 1. This suggests that the flipping of the methylene bridge in compound 5 is slower in a more acidic solvent; just the same trend as is clearly shown by compound 4, although the methylene signal of compound 5 in D₂SO₄ appears as a singlet even at ~0 °C.

Electronic Spectra of Compounds 4–9.—The electronic absorption maxima of the annulenediones 4–9, determined in both tetrahydrofuran (THF) and sulfuric acid, are listed in Table 3, and the absorption spectra of the [24]- 5, [26]- 6, [28]- 7, and [30]-annulenedione 8 are illustrated in Fig. 2. As seen from Fig. 2, the spectra of the potentially [4*n*] π -electron systems, [26]- 6 and [30]-annulenedione 8, and those of the potentially [4*n* + 2] π -electron system, [24]- 5 and [28]-annulenedione 7, are similar in shape, and differ only in the bathochromic shift of each band. Also, the spectra of compounds 6 and 8 exhibit some broadening of the absorption curves, as compared with the spectra of compounds 5 and 7, as has been observed for the tetrahydroannulenediones 1^{1,2} and for the carbocyclic annulenes,¹⁹ albeit they have little annulene character (see below).

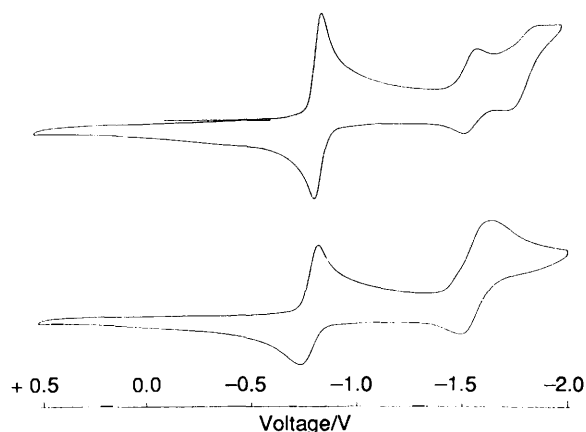
It is recognized that the electronic spectra of the annulenes¹⁹ and dehydroannulenediones 1^{1,2} have been shown to alternate, the main absorption maxima (the strongest maxima) of (4*n* + 2) π -electron systems being at higher wavelength than those of (4*n*) systems.²⁰ However, Table 3 shows that the main absorption maxima of compounds 4–9 in THF exhibit a bathochromic shift as the ring size increases, and the alternation of the maxima is not exhibited for these annulenedione series, reflecting the fact that compounds 4–9 have little annulene character, as is revealed by their ¹H NMR spectra (see above).

Also, it is evident from Table 3 that all the bands of compounds 4–9 show a very large bathochromic shift (100–200 nm) in every case on changing the solvent from THF to H₂SO₄, reflecting the degree of extended conjugation of the respective π -electron system. Unfortunately, the spectra of compounds 6–8 changed with the elapse of time (see the text on the ¹H NMR spectra), and it was not possible to use the main maxima of compounds 6–8 for comparison with regard to the above discussion on the alternation.

Redox Property of Compounds 4–9.—The redox behaviour of the annulenediones 4–9 as well as that of the acyclic diketone 16 was studied by cyclic voltammetry in organic solvents. The redox potentials obtained in dimethyl sulfoxide (DMSO) are listed in Table 4. Voltammograms of compounds 5 and 9 are shown in Fig. 3.

Table 4 Redox potentials of compounds 4–9 and 16

Compound	$E_{\frac{1}{2}}^1$	$E_{\frac{1}{2}}^2$	$E_{\frac{1}{2}}^3$	$E_{\frac{1}{2}}^2 - E_{\frac{1}{2}}^3$
[20]- 4	-0.99	-1.78	-1.93 ^a	0.15
[24]- 5	-0.83	-1.53	-1.74	0.21
[26]- 6	-0.82	-1.65	-1.95 ^a	0.30
[28]- 7	-0.80	-1.54	-1.74	0.20
[30]- 8	-0.76	-1.60	-1.75	0.15
[32]- 9	-0.76	-1.52		0.00
16	-0.99			

^a Half-wave reduction potentials.**Fig. 3** Cyclic voltammograms of compounds 5 (upper) and 9 (lower) at room temperature (scan rate, 60 mV sec⁻¹)

The acyclic diketone 16 gives a single reversible redox wave irrespective of the sweep rates and the solvents, while the annulenediones 4–8 give three reduction waves ($E_{\frac{1}{2}}^1$, $E_{\frac{1}{2}}^2$ and $E_{\frac{1}{2}}^3$), the peak heights being in the proportions 2:1:1. As the ring size increases, the second and third waves tend to coalesce and in the largest-membered, [32]annulenedione 9, only two pairs of redox waves are observed.

The first wave is assigned to two-electron transfer to form a dianion, and the second and third waves to two successive one-electron-transfer reactions to form up to a tetraanion probably involving the diyne moiety.

The first redox potential of the [20]annulenedione 4 is the same as that of the acyclic diketone 16 and is higher than those of compounds 5–9, which may be due to the lower planarity of the molecular skeleton of compound 4, suggesting little contribution for peripheral π -electron conjugation through the diacetylenic linkage. On the other hand, the larger membered annulenediones 5–9 are reduced more readily to form the corresponding dianions than is compound 4. This fact indicates that the diacetylene linkage participates in the peripheral conjugation to stabilize the dianion. Interestingly, the second redox potential ($E_{\frac{1}{2}}^2$) alternates among compounds 5–9, reflecting the ease of the second step to form the trianion radical depending on the ring size. The dianions having $(4n)\pi$ -electrons (5^{2-} , 7^{2-} and 9^{2-}) are more easily reduced to the corresponding trianion radicals than are the dianions having $(4n + 2)\pi$ -electrons (6^{2-} and 8^{2-}) (see Scheme 2). As is seen from Table 4, the difference between $E_{\frac{1}{2}}^2$ and $E_{\frac{1}{2}}^3$ is relatively small and decreases with increasing ring size. This effect may be understood in terms of electrostatic repulsion, since the energy required for adding one electron to a trianion radical is smaller with a larger ring size.

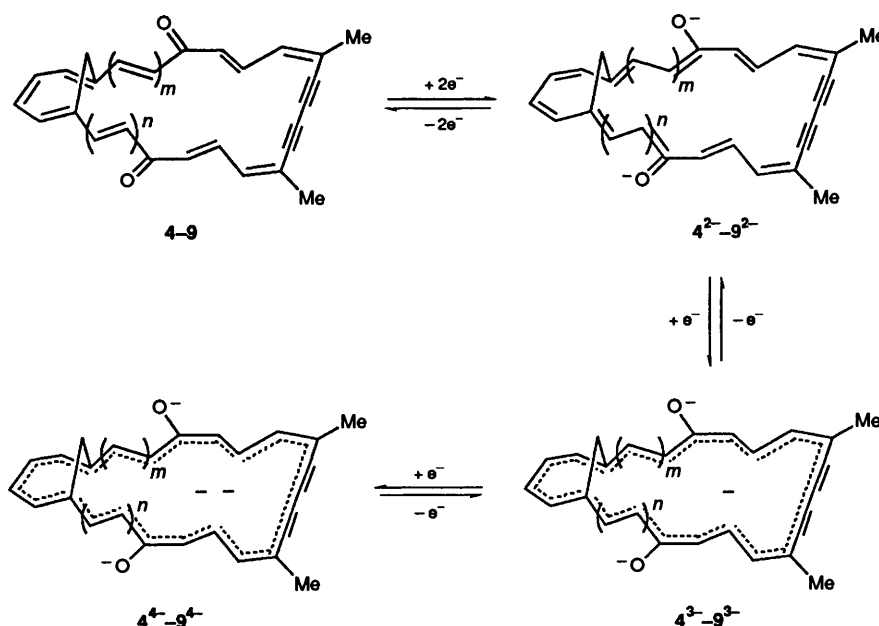
Experimental

M.p.s were determined on a hot-stage apparatus and are

uncorrected. IR spectra were taken with a Hitachi 260–50 spectrophotometer as KBr discs and were calibrated against polystyrene; only significant maxima are described. Electronic spectra were measured in THF and sulfuric acid solutions, and run with a Hitachi 220A or a Shimadzu UV-160 spectrophotometer. Mass spectra were recorded with a JEOL JMS-D 300 spectrometer operating at 75 eV using a direct-inlet system or a JMS-D spectrometer equipped with a field-desorption system unless otherwise stated. Fast-atom-bombardment mass spectra (FAB-MS) were obtained on a JEOL JMS-AX 505W high-resolution double-focusing mass spectrometer equipped with a D 5000 data system. Ions were generated by bombardment of the target matrix with a neutral xenon atom beam (derived from a Xe⁺ ion beam accelerated at 2 kV). Samples for FAB-MS were prepared by dissolving the compounds in a *m*-nitrobenzyl alcohol matrix. ¹H NMR spectra at ambient temperature were recorded as CDCl₃ solutions with a JEOL FX-90Q, a JEOL GX-270, a Bruker AM-360 or a Bruker AM-500 spectrometer at 89.60, 270.16, 360.13 or 500.14 MHz, respectively. Internal SiMe₄ was used as a reference when the solvent was CDCl₃ or CF₃CO₂D, while external SiMe₄ was used when the solvent was D₂SO₄. *J*-Values are given in Hz. Variable-temperature ¹H NMR measurements were made on the AM-500 and the temperatures were calibrated with either an ethylene glycol sample or a methanol one. ¹³C NMR spectra were recorded as CDCl₃ solution on the AM-500 at 125.76 MHz with internal SiMe₄ as a reference. Cyclic voltammetry was determined on a BAS CV-27 potentiostat and function generator and was carried out at a sweep rate of 60 mV s⁻¹ in DMSO containing 0.1 mol dm⁻³ tetrabutylammonium perchlorate, using Ag/AgCl as a reference electrode and platinum as a working electrode.

Aq. sodium hydroxide (1.18 mol dm⁻³) was used for the aldol condensations of the dialdehydes 10–14 with acetone. Ethanolic sodium ethoxide (2.17 mol dm⁻³) was used for the aldol condensations of compounds 15–20 with the aldehyde 21 and was prepared from sodium (1.50 g) and dry ethanol (25 cm³) immediately before use. The preparations of the acyclic diketones 22–27 were carried out under argon. Merck alumina (activity II–III), Merck silica gel 60 or Daiso gel 1001 W were used for column chromatography. Compounds were pre-adsorbed from hexane, diethyl ether or benzene solution onto the adsorbent before column chromatography. Progress of all reactions was followed by TLC on Merck precoated silica gel. Organic extracts were washed with saturated aq. sodium chloride and dried over anhydrous sodium sulfate prior to removal of solvent. Solvents were evaporated under water-pump pressure. Ether refers to diethyl ether.

1,6-Bis(5-methyl-1-oxohepta-2,4-dien-6-ynyl)cyclohepta-1,3,5-triene 22.—To a stirred solution of the diketone 15¹¹ (2.00 g, 11.4 mmol) and the aldehyde 21¹² (5.30 g, 56.8 mmol) in dry benzene (396 cm³) at 6 °C was added dropwise by syringe during 2 h a mixture of ethanolic sodium ethoxide (6.0 cm³) in dry benzene (12.0 cm³). After the mixture had been stirred for 30 min, a further quantity of ethanolic sodium ethoxide (3.0 cm³) in dry benzene (6.0 cm³) was added dropwise during 1 h at 6 °C. After being stirred for a further 1.5 h, the reaction mixture was poured onto ice-cooled, saturated aq. ammonium chloride (400 cm³)–benzene (300 cm³), and the aqueous layer was extracted with benzene. The combined organic layer was washed with aq. sodium hydrogen carbonate and dried. The yellow liquid obtained after removal of solvent was chromatographed on silica gel (4.2 × 10.8 cm). The fractions eluted with 30–60% dichloromethane in benzene afforded the acyclic diketone 22 (1.64 g, 44%) as pale yellow needles, m.p. 103–104 °C (decomp.) (from hexane–benzene); *m/z* 328 (M⁺, 13%) and 65 (100 (Found: M, 328.3); λ_{\max}/nm 323 ($\epsilon/\text{dm}^3 \text{ mol}^{-1}$



cm^{-1} 28 400); $\nu_{\text{max}}/\text{cm}^{-1}$ 3270 (C≡CH), 2080 (C≡C), 1640 (C=O) and 985 (E-HC=CH); δ_{H} (90 MHz) 7.78 (2 H, dd, J 15 and 11, H^B), 7.26 (2 H, m, H²), 6.94 (2 H, m, H¹), 6.95 (2 H, d, J 15, H^C), 6.51 (2 H, d, J 11, H^A), 3.47 (2 H, s, C≡CH), 3.08 (2 H, s, CH₂) and 2.03 (6 H, s, Me) (Found: C, 83.9; H, 6.2. C₂₃H₂₀O₂ requires C, 84.1; H, 6.1%).

12,13,14,15-Tetradehydro-11,16-dimethyl-1,6-methano[20]-annulene-7,20-dione **4**.—A solution of compound **22** (0.50 g, 1.53 mmol) in pyridine-ether (3:1; 160 cm³) was added dropwise during 6 h to a stirred solution of anhydrous copper(II) acetate (10.0 g) in pyridine-ether (3:1; 240 cm³) at 50 °C, and the mixture was stirred for a further 30 min at the same temperature. Then the mixture was poured onto water and extracted with benzene. The combined extracts were washed successively with 5% HCl until they turned acidic to litmus, and then with aq. sodium hydrogen carbonate, and were then dried and concentrated. The residue was chromatographed on silica gel (3.0 × 9.0 cm). The fractions eluted with 30–40% dichloromethane in benzene afforded the tetradehydro-[20]annulenedione **4** (292 mg, 58%) as pale yellow needles, m.p. 195 °C (decomp.) (from dichloromethane); m/z 326 (M⁺, 5%) and 90 (100) (Found: M, 326.3); for UV data see Table 3; $\nu_{\text{max}}/\text{cm}^{-1}$ 2200 (C≡C), 1630 (C=O) and 980 (E-HC=CH); δ_{H} (500 MHz; CDCl₃; -36 °C) 7.14 (2 H, dd, J 16.0 and 11.1, H^B), 7.06 (2 H, m, H²), 6.95 (2 H, m, H¹), 6.65 (2 H, d, J 11.1, H^A), 6.23 (2 H, d, J 16.0, H^C), 4.18 (1 H, d, J 13.7, CH₂), 1.96 (6 H, s, Me) and 1.93 (1 H, d, J 13.7, CH₂); δ_{H} (500 MHz; CF₃CO₂D; 26 °C) 7.56 (2 H, dd, J 15.7 and 11.1, H^B), 7.29 (2 H, m, H²), 7.13 (2 H, m, H¹), 6.76 (2 H, d, J 11.1, H^A), 6.45 (2 H, d, J 15.7, H^C), 4.18 (1 H, br s, CH₂), 2.22 (1 H, br s, CH₂) and 2.03 (6 H, s, Me); δ_{H} (500 MHz; D₂SO₄; 26 °C) 7.28 (2 H, m, H²), 7.14 (2 H, m, H¹), 7.12 (2 H, d, J 10.9, H^A), 6.94 (2 H, dd, J 13.9 and 10.9, H^B), 6.68 (2 H, d, J 13.9, H^C), 3.89 (1 H, d, J 14.0, CH₂), 2.38 (1 H, d, J 14.0, CH₂) and 2.12 (6 H, s, Me). See also Tables 1 and 2; δ_{C} (125 MHz) 194.7 (C=O), 141.1 (t), 138.8 (t), 136.4 (q), 134.6 (t), 134.5 (t), 130.0 (t), 126.4 (q), 85.5 (≡C), 82.1 (≡C), 23.1 (CH₂) and 21.5 (2 × Me) (Found: C, 84.7; H, 5.7. C₂₃H₁₈O₂ requires C, 84.6; H, 5.6%).

1,6-Bis(3-oxobut-1-enyl)cyclohepta-1,3,5-triene **16**.—Aq. sodium hydroxide (17 cm³) was added dropwise to a stirred

solution of the dialdehyde **10**¹¹ (0.50 g, 3.40 mmol) in acetone (26 cm³) during 40 min at 5 °C. After the mixture had been stirred for a further 2 h at 5 °C, the reaction was terminated by addition of acetic acid. Then the mixture was poured onto water and extracted with benzene. The extracts were washed with aq. sodium hydrogen carbonate and dried. The residual dark red liquid obtained after removal of solvent was chromatographed on silica gel (3.2 × 13.5 cm). The fractions eluted with benzene-dichloromethane (1:1) afforded the diketone **16** (538 mg, 69%) as yellow needles, m.p. 108–110 °C (from hexane-benzene); m/z 228 (M⁺, 100%) (Found: M, 228.2); $\lambda_{\text{max}}/\text{nm}$ 253 (ϵ /11 700), 259sh (16 400), 281 (53 500) and 372 (8750); $\nu_{\text{max}}/\text{cm}^{-1}$ 1660 (C=O), 1610 (C=C) and 980 (E-HC=CH); δ_{H} (90 MHz) 7.26 (2 H, d, J 16, H^A), 6.80 (2 H, m, H²), 6.64 (2 H, m, H¹), 6.46 (2 H, d, J 16, H^B), 2.70 (2 H, s, CH₂) and 2.34 (6 H, s, Me) (Found: C, 78.8; H, 7.0. C₁₅H₁₆O₂ requires C, 78.9; H, 7.1%).

1,6-Bis(7-methyl-3-oxonona-1,4,6-trien-8-ynyl)cyclohepta-1,3,5-triene **23**.—To a solution of the diketone **16** (0.30 g, 1.3 mmol) and the aldehyde **21** (1.01 g, 10.6 mmol) in dry benzene (47 cm³) at 5 °C was added dropwise during 30 min a mixture of ethanolic sodium ethoxide (1.0 cm³) in dry benzene (2.0 cm³). After the mixture had been stirred for 2 h, a further quantity of ethanolic sodium ethoxide (1.0 cm³) in dry benzene (2.0 cm³) was added dropwise during 30 min at 5 °C. After being stirred for 2 h, the mixture was worked up as for the isolation of compound **22**. The product was chromatographed on silica gel (3.2 × 10 cm). The fractions eluted with 5% dichloromethane in benzene afforded the acyclic diketone **23** (266 mg, 54%) as orange needles, m.p. 146–148 °C (decomp.) (from hexane-benzene); m/z 381 (M⁺ + 1) (FAB method) (Found: M, 380.4; $\lambda_{\text{max}}/\text{nm}$ 249 (ϵ 24 500), 339 (49 400) and 393sh (12 400); $\nu_{\text{max}}/\text{cm}^{-1}$ 3250 (C≡CH), 2100 (C≡C), 1660, 1640 (C=O), 1600 (C=C), 1000 and 990 (E-HC=CH); δ_{H} (360 MHz) 7.75 (2 H, dd, J 15.3 and 11.3, H^B), 7.41 (2 H, d, J 15.6, H^E), 6.80 (2 H, m, H²), 6.76 (2 H, d, J 15.6, H^D), 6.66 (2 H, m, H¹), 6.49 (2 H, d, J 15.3, H^C), 6.48 (2 H, d, J 11.3, H^A), 3.53 (2 H, s, C≡CH), 2.78 (2 H, s, CH₂) and 2.05 (6 H, s, Me) (Found: C, 85.45; H, 6.5. C₂₇H₂₄O₂ requires C, 85.2; H, 6.4%).

14,15,16,17-Tetradehydro-13,18-dimethyl-1,6-methano[24]-annulene-9,22-dione **5**.—This reaction was performed using a

high-dilution apparatus. A solution of compound **23** (0.70 g, 1.9 mmol) in ether (135 cm³)–methanol (15 cm³) was added dropwise during 5 h to a stirred and refluxing solution of copper(II) acetate monohydrate (1.62 g) in a mixture of pyridine (45 cm³), methanol (90 cm³) and ether (135 cm³) at 50 °C. After being refluxed and stirred for a further 1 h, the mixture was worked up as for the isolation of compound **4**. The product was chromatographed on silica gel (3.2 × 10 cm). The fractions eluted with benzene–dichloromethane (4:1) afforded the *tetrahydro[24]annulenedione 5* (260 mg, 36%) as orange needles, m.p. 148–150 °C (decomp.) (from hexane–benzene); *m/z* 378 (M⁺, 20%) and 153 (100) (Found: M, 378.4); for UV data see Table 3 and Fig. 2; $\nu_{\max}/\text{cm}^{-1}$ 2200 (C≡C), 1645 (C=O), 1610 (C=C) and 990 (E-HC=CH); δ_{H} (500 MHz) 7.53 (2 H, d, *J* 15.3, H^E), 7.22 (2 H, dd, *J* 16.1 and 10.2, H^B), 6.68 (4 H, m, H¹ and H²), 6.65 (2 H, d, *J* 15.3, H^D), 6.61 (2 H, br d, *J* 10.2, H^A), 6.55 (2 H, d, *J* 16.1, H^C), 2.80 (2 H, s, CH₂) and 2.11 (6 H, s, Me); see also Fig. 1; δ_{H} (500 MHz; CF₃CO₂D; 26 °C) 8.27 (2 H, d, *J* 15.1, H^E), 7.29 (2 H, t, *J* 3.6, H²), 7.22–7.12 (6 H, m, H^A, H^B and H¹), 6.97 (2 H, m, H^C), 6.30 (2 H, d, *J* 15.1, H^D), 2.50 (2 H, s, CH₂) and 2.39 (6 H, s, Me); see also Fig. 1; δ_{H} (500 MHz; D₂SO₄; 26 °C) 8.86 (2 H, d, *J* 14.6, H^E), 7.61 (2 H, m, H²), 7.46 (2 H, *J* 11, H^A), 7.19 (2 H, m, H¹), 6.91 (2 H, br s, H^C), 5.10 (2 H, br s, H^B), 3.93 (2 H, d, *J* 14.6, H^D), 2.29 (6 H, s, Me) and 0.53 (2 H, s, CH₂); see also Fig. 1; δ_{C} (125 MHz) 190.1 (C=O), 146.1 (t), 137.8 (t), 137.7 (t), 136.7 (t), 133.5 (t), 132.8 (q), 132.3 (t), 125.7 (q), 84.3 (≡C), 82.3 (≡C), 25.5 (CH₂) and 23.4 (Me) (Found: C, 85.6; H, 6.05. C₂₇H₂₂O₂ requires C, 85.7; H, 5.9%).

1-(3-Oxobut-1-enyl)-6-(3-oxohexa-1,3-dienyl)cyclohepta-1,3,5-triene **17**.—Aq. sodium hydroxide (29 cm³) was added dropwise to a stirred solution of the dialdehyde **11** (1.00 g, 5.74 mmol) in acetone (44 cm³) during 1 h at 3 °C. After being stirred for a further 1.5 h at 3 °C, the mixture was worked up as for the isolation of compound **16**. The product was chromatographed on alumina (3.2 × 6.0 cm). The fractions eluted with 40–50% ether in hexane afforded the *diketone 17* 1.08 g, 74%) as yellow needles, m.p. 81–82 °C (decomp.) (from hexane–benzene); *m/z* 254 (M⁺, 100%) (Found: M, 254.3); λ_{\max}/nm 291sh (ϵ 37 300), 300 (46 800) and 394 (9 400); $\nu_{\max}/\text{cm}^{-1}$ 1660 (C=O), 1600 (C=C) and 990 (E-HC=CH); δ_{H} (500 MHz) 7.25 (1 H, d, *J* 16.0, H^B), 7.22 (1 H, dd, *J* 15.4 and 9.1, H^B), 6.77 (1 H, dd, *J* 11.0 and 6.1, H²), 6.74–6.69 (3 H, m, H^C, H^D and H³), 6.62 (1 H, d, *J* 6.1, H⁴), 6.47 (1 H, d, *J* 6.1, H¹), 6.43 (1 H, d, *J* 16.0, H^A), 6.33 (1 H, d, *J* 15.4, H^A), 2.72 (2 H, s, CH₂), 2.33 (3 H, s, Me) and 2.30 (3 H, s, Me) (Found: C, 80.0; H, 6.9. C₁₇H₁₈O₂ requires C, 80.3; H, 7.1%).

1-(7-Methyl-3-oxonona-1,4,6-trien-8-ynyl)-6-(9-methyl-5-oxoundeca-1,3,6,8-tetraen-10-ynyl)cyclohepta-1,3,5-triene **24**.—To a stirred solution of the diketone **17** (0.30 g, 1.17 mmol) and the aldehyde **21** (0.95 g, 10.1 mmol) in dry benzene (60 cm³) at 6 °C was added dropwise during 30 min a mixture of ethanolic sodium ethoxide (1.0 cm³) in dry benzene (2.0 cm³). After the mixture had been stirred for 1 h, a further quantity of ethanolic sodium ethoxide (2.0 cm³) in dry benzene (4.0 cm³) was added dropwise during 1 h at 6 °C. After being stirred for 2.5 h, the mixture was worked up as for the isolation of compound **22**. The product was chromatographed on silica gel (3.2 × 9.0 cm). The fractions eluted with benzene–dichloromethane (4:1) afforded the acyclic *diketone 24* (239 mg, 50%) as orange needles, m.p. 95–97 °C (decomp.) (from hexane–benzene); no satisfactory mass spectra could be obtained by direct-inlet method; λ_{\max}/nm 267 (ϵ 29 700), 349 (56 300) and 422 (16 900); $\nu_{\max}/\text{cm}^{-1}$ 3290 (C≡CH), 2100 (C≡C), 1660, 1640 (C=O) and 985 (E-HC=CH); δ_{H} (500 MHz) 7.76 (1 H, dd, *J* 15.3 and 11.3, H^B), 7.71 (1 H, dd, *J* 15.4 and 11.3, H^B), 7.40 (1 H, d, *J* 15.6, H^E), 7.37 (1 H, dd, *J* 15.6 and 9.3, H^E), 6.79–6.70 (5 H, m, H^D, H^F, H^G, H²

and H³), 6.65 (1 H, d, *J* 15.6, H^D), 6.64 (1 H, d, *J* 7.8, H⁴), 6.50–6.45 (4 H, m, H^A, H^C and H¹), 6.42 (1 H, d, *J* 15.4, H^C), 3.53 (2 H, s, C≡CH), 2.78 (2 H, s, CH₂) and 2.05 (6 H, s, Me) (Found: C, 85.6; H, 6.6. C₂₉H₂₆O₂ requires C, 85.7; H, 6.45%).

14,15,16,17-Tetrahydro-13,18-dimethyl-1,6-methano[26]-annulene-9,22-dione **6**.—The reaction was performed with a high-dilution apparatus. To a refluxing solution of copper(II) acetate monohydrate (4.0 g) in a mixture of pyridine (267 cm³), methanol (40 cm³) and ether (200 cm³) at 58 °C was added dropwise during 6.5 h a solution of compound **24** (0.38 g, 0.94 mmol) in a mixture of pyridine (133 cm³), methanol (26 cm³) and ether (60 cm³). After being refluxed and stirred for a further 1 h, the mixture was worked up as for the isolation of compound **4**. The product was chromatographed on silica gel (3.2 × 9.0 cm). The fractions eluted with benzene–dichloromethane (1:4) afforded the *tetrahydro[26]annulenedione 6* (155 mg, 41%) as red needles, m.p. 215–220 °C (decomp.) (from hexane–THF); *m/z* 404 (M⁺, 38%) and 165 (100) (Found: M, 404.4); for UV data see Table 3 and Fig. 2; $\nu_{\max}/\text{cm}^{-1}$ 2200 (C≡C), 1640 (C=O), 1000 and 980 (E-HC=CH); δ_{H} (500 MHz) 7.79 (1 H, dd, *J* 16.1 and 11.1, H^B), 7.44 (1 H, dd, *J* 16.0 and 10.7, H^B), 7.36 (1 H, d, *J* 15.4, H^E), 7.34 (1 H, dd, *J* 14.9 and 11.0, H^E), 7.15 (1 H, d, *J* 14.9, H^D), 7.01 (1 H, d, *J* 15.4, H^D), 6.90 (1 H, dd, *J* 15.1 and 11.0, H^F), 6.71 (1 H, d, *J* 15.1, H^G), 6.66–6.57 (3 H, m, H², H³ and H⁴), 6.54 (1 H, d, *J* 11.1, H^A), 6.46 (1 H, d, *J* 16.0, H^C), 6.44 (1 H, d, *J* 10.7, H^A), 6.37 (1 H, d, *J* 6.3, H¹), 6.19 (1 H, d, *J* 16.1, H^C), 3.04 (2 H, s, CH₂), 2.07 (3 H, s, Me^b) and 2.05 (3 H, s, Me^a); δ_{C} (125 MHz) 190.9 (C=O), 189.8 (C=O), 145.7 (t), 143.6 (t), 143.2 (t), 139.7 (t), 138.2 (t), 137.5 (t), 136.7 (t), 136.6 (t), 133.9 (t), 133.5 (t), 133.1 (t), 132.7 (q), 132.3 (t), 132.2 (q), 131.6 (t), 127.4 (q), 126.7 (t), 125.0 (q), 124.4 (t), 122.6 (t), 84.1 (≡C), 83.5 (≡C), 82.3 (≡C), 26.4 (CH₂), 24.2 (Me) and 23.0 (Me) (Found: C, 85.85; H, 6.2. C₂₉H₂₄O₂ requires C, 86.1; H, 6.0%).

1,6-Bis(5-oxohexa-1,3-dienyl)cyclohepta-1,3,5-triene **18**.—Aq. sodium hydroxide (57 cm³) was added dropwise to a stirred solution of the dialdehyde **12** (1.42 g, 7.1 mmol) in acetone (57 cm³) during 1 h at 3 °C. After being stirred for a further 30 min at 3 °C, the mixture was worked up as for the isolation of compound **16**. The product was chromatographed on alumina (4.2 × 6.0 cm). The fractions eluted with 10% hexane in ether afforded the *diketone 18* (1.48 g, 74%) as orange needles, m.p. 127–128 °C (from hexane–benzene); *m/z* 280 (M⁺, 100%) (Found: M, 280.3); λ_{\max}/nm 317 (ϵ 87 200) and 415 (14 500); $\nu_{\max}/\text{cm}^{-1}$ 1650 (C=O), 1600 (C=C) and 995 (E-HC=CH); δ_{H} (270 MHz) 7.22 (2 H, dd, *J* 15 and 10, H^C), 6.74 (2 H, d, *J* 15, H^A), 6.71 (2 H, m, H²), 6.64 (2 H, dd, *J* 15 and 10, H^B), 6.46 (2 H, m, H¹), 6.27 (2 H, d, *J* 15, H^D), 2.74 (2 H, s, CH₂) and 2.31 (6 H, s, Me) (Found: C, 81.6; H, 7.0. C₁₉H₂₀O₂ requires C, 81.4; H, 7.2%).

1,6-Bis(9-methyl-5-oxoundeca-1,3,6,8-tetraen-10-ynyl)cyclohepta-1,3,5-triene **25**.—A mixture of ethanolic sodium ethoxide (1.7 cm³) in dry benzene (3.4 cm³) was added dropwise to a solution of the diketone **18** (420 mg, 1.5 mmol) and the aldehyde **21** (1.05 g, 12 mmol) in dry benzene (54 cm³) during 1.5 h at 5 °C. After being stirred for 1 h at 5 °C, the mixture was worked up as for the isolation of compound **22**. The product was chromatographed on silica gel (3.8 × 10.5 cm). The fractions eluted with benzene–dichloromethane (1:1) afforded the acyclic *diketone 25* (550 mg, 85%) as red needles, m.p. 118–119 °C (decomp.) (from hexane–THF); no satisfactory mass spectra could be obtained using direct-inlet method; λ_{\max}/nm 278 (ϵ 25 900), 360 (53 400) and 437 (13 100); $\nu_{\max}/\text{cm}^{-1}$ 3290, 3250 (C≡CH), 2100 (C≡C), 1660, 1640 (C=O), 1600 (C=C) and 1000 (E-HC=CH); δ_{H} (500 MHz) 7.71 (2 H, dd, *J* 15.5 and 11.2, H^B), 7.38 (2 H, dd, *J* 15.1 and 9.8, H^E), 6.79–6.73 (4 H, m, H^F and

H^c), 6.67 (2 H, m, H²), 6.57 (2 H, d, *J* 15.1, H^D), 6.50–6.46 (6 H, m, H^A, H^C and H¹), 3.59 (2 H, s, C≡CH), 2.77 (2 H, s, CH₂) and 2.04 (6 H, s, Me) (Found: C, 85.8; H, 6.5. C₃₁H₂₈O₂ requires C, 86.1; H, 6.5%).

16,17,18,19-Tetradehydro-15,20-dimethyl-1,6-methano[28]-annulene-11,24-dione **7**.—A solution of compound **25** (1.70 g, 4.05 mmol) in pyridine-ether (3:1; 400 cm³) was added dropwise during 5.5 h to a stirred solution of anhydrous copper(II) acetate (24.0 g) in pyridine-ether (3:1; 600 cm³) at 50 °C. After being stirred for a further 1 h, the mixture was worked up as for the isolation of compound **4**. The product was chromatographed on silica gel (3.8 × 11.0 cm). The fractions eluted with benzene-dichloromethane (1:1) afforded the tetradehydro[28]annulenedione **7** (606 mg, 36%) as red needles, m.p. 258–260 °C (from hexane-THF); *m/z* 430 (M⁺, 33%) and 178 (100) (Found: M, 430.5); for UV data see Table 3 and Fig. 2; $\nu_{\max}/\text{cm}^{-1}$ 2150 (C≡C), 1640 (C=O) and 1000 (E-HC=CH); δ_{H} (500 MHz) 7.59 (2 H, dd, *J* 14.8 and 11.3, H^E), 7.27 (2 H, dd, *J* 16.0 and 11.0, H^B), 6.92 (2 H, d, *J* 15.0, H^G), 6.86 (2 H, d, *J* 14.8, H^D), 6.69 (2 H, m, H²), 6.62 (2 H, dd, *J* 15.0 and 11.3, H^F), 6.59 (2 H, d, *J* 11.0, H^A), 6.52 (2 H, m, H¹), 6.34 (2 H, d, *J* 16.0, H^C), 2.74 (2 H, s, CH₂) and 2.16 (6 H, s, Me); δ_{C} (125 MHz) 190.9 (C=O), 189.8 (C=O), 145.7 (t), 143.6 (t), 143.2 (t), 139.7 (t), 138.2 (t), 137.5 (t), 136.6 (t), 136.6 (t), 133.9 (t), 133.5 (t), 133.1 (t), 132.7 (q), 132.3 (t), 132.2 (q), 131.6 (t), 127.4 (q), 126.7 (t), 125.0 (q), 124.4 (t), 122.6 (t), 84.1 (≡C), 83.5 (≡C), 82.3 (≡C), 82.3 (≡C), 26.4 (CH₂), 24.2 (Me) and 23.0 (Me) (Found: C, 86.45; H, 6.3. C₃₁H₂₆O₂ requires C, 86.5; H, 6.1%).

1-(5-Oxohexa-1,3-dienyl)-6-(7-oxoocta-1,3,5-trienyl)cyclohepta-1,3,5-triene **19**.—Aq. sodium hydroxide (33 cm³) was added dropwise during 1 h to a stirred solution of the dialdehyde **13** (1.23 g, 5.4 mmol) in acetone (40 cm³) at 3 °C. After being stirred for a further 1 h at 3 °C, the mixture was worked up as for the isolation of compound **16**. The product was chromatographed on alumina (3.8 × 6.5 cm). The fractions eluted with benzene-dichloromethane (1:1) afforded the diketone **19** (1.17 g, 70%) as red needles, m.p. 126–128 °C (decomp.) (from hexane-benzene); *m/z* 306 (M⁺, 21%) and 69 (100) (Found: M, 306.3); λ_{\max}/nm 335 (ϵ 88 500) and 430 (17 800); $\nu_{\max}/\text{cm}^{-1}$ 1660 (C=O), 1590 (C=C) and 1000 (E-HC=CH); δ_{H} (500 MHz) 7.22 (1 H, dd, *J* 15.5 and 10.6, H^B), 7.20 (1 H, dd, *J* 15.5 and 11.3, H^B), 6.76–6.62 (6 H, m, H^D, H^D, H^E, H², H³ and H⁴), 6.56 (1 H, d, *J* 14.7, H^F), 6.49–6.41 (2 H, m, H^C and H^C), 6.41 (1 H, d, *J* 6.0, H¹), 6.24 (2 H, d, *J* 15.5, H^A and H^A), 2.74 (2 H, s, CH₂), 2.31 (3 H, s, Me) and 2.29 (3 H, s, Me) (Found: C, 82.3; H, 7.1. C₂₁H₂₂O₂ requires C, 82.3; H, 7.2%).

1-(9-Methyl-5-oxoundeca-1,3,6,8-tetraen-10-ynyl)-6-(11-methyl-7-oxotrideca-1,3,5,8,10-pentaen-12-ynyl)cyclohepta-1,3,5-triene **26**.—A mixture of ethanolic sodium ethoxide (1.8 cm³) in dry benzene (3.6 cm³) was added dropwise to a solution of the diketone **19** (0.55 g, 1.80 mmol) and the aldehyde **21** (1.64 g, 17.4 mmol) in dry benzene (100 cm³) at 4 °C. After being stirred for 1 h at 4 °C, the mixture was worked up as for the isolation of compound **22**. The product was chromatographed on silica gel (4.2 × 7.0 cm). The fractions eluted with ether-dichloromethane (1:9) afforded the acyclic diketone **26** (335 mg, 41%) as red needles, m.p. 121–122 °C (decomp.) (from hexane-benzene); no satisfactory mass spectra could be obtained using direct-inlet method; λ_{\max}/nm 281sh (ϵ 33 100), 373 (72 000) and 451 (22 500); $\nu_{\max}/\text{cm}^{-1}$ 3290, 3225 (C≡CH), 2100 (C≡C), 1660, 1640 (C=O), 1600 (C=C) and 1000 (E-HC=CH); δ_{H} (500 MHz) 7.71 (1 H, dd, *J* 15.5 and 11.3, H^B), 7.69 (1 H, dd, *J* 15.3 and 11.3, H^B), 7.38 (1 H, dd, *J* 15.3 and 9.9, H^E), 7.36 (1 H, dd, *J* 15.2 and 11.7, H^E), 6.78–6.40 (16 H, m, olefinic H), 3.51 (1 H, s,

C≡CH), 3.50 (1 H, s, C≡CH), 2.76 (2 H, s, CH₂) and 2.04 (6 H, s, Me) (Found: C, 86.5; H, 6.7. C₃₃H₃₀O₂ requires C, 86.4; H, 6.6%).

16,17,18,19-Tetradehydro-15,20-dimethyl-1,6-methano[30]-annulene-11,24-dione **8**.—A solution of compound **26** (300 mg, 0.654 mmol) in pyridine-ether (3:1; 600 cm³) was added dropwise during 8 h to a stirred solution of anhydrous copper(II) acetate (6.0 g) in pyridine-ether (3:1; 400 cm³) at 52 °C. After being stirred for a further 1 h at 52 °C, the mixture was worked up as for the isolation of compound **4**. The product was chromatographed on silica gel (3.2 × 9.0 cm). The fractions eluted with benzene-dichloromethane (1:4) afforded the tetradehydro[30]annulenedione **8** (182 mg, 61%) as purple needles, m.p. 288–294 °C (decomp.) (from hexane-THF); *m/z* 456 (M⁺, 30%) and 57 (100) (Found: M, 456.5); for UV data see Table 3 and Fig. 2; $\nu_{\max}/\text{cm}^{-1}$ 2180 (C≡C), 1640 (C=O), 1600 (C=C) and 1000 (E-HC=CH); δ_{H} (500 MHz) 8.07 (1 H, dd, *J* 15.8 and 11.5, H^E), 7.76 (1 H, dd, *J* 15.0 and 11.5, H^B), 7.75 (1 H, dd, *J* 16.1 and 11.1, H^B), 7.38 (1 H, dd, *J* 14.8 and 11.6, H^F), 7.17 (1 H, d, *J* 14.8, H^D), 7.14 (1 H, dd, *J* 15.2 and 10.4, H^H), 7.06 (1 H, dd, *J* 14.6 and 11.6, H^F), 6.72 (1 H, dd, *J* 14.6 and 10.4, H^G), 6.62 (1 H, m, H³), 6.62 (1 H, d, *J* 15.8, H^D), 6.58 (1 H, m, H²), 6.54 (1 H, m, H^F), 6.53 (1 H, d, *J* 15.2, H¹), 6.53 (1 H, d, *J* 11.1, H^A), 6.45 (1 H, d, *J* 11.5, H^A), 6.41 (1 H, d, *J* 6.1, H⁴), 6.40 (1 H, d, *J* 15.0, H^C), 6.34 (1 H, d, *J* 6.1, H¹), 6.20 (1 H, d, *J* 16.1, H^C), 6.09 (1 H, d, *J* 11.1, H^G), 2.94 (2 H, s, CH₂), 2.07 (3 H, s, Me^a) and 2.05 (3 H, s, Me^b); δ_{C} (125 MHz) 189.9 (C=O), 189.6 (C=O), 144.9 (t), 143.8 (t), 143.5 (t), 143.3 (t), 139.2 (t), 138.8 (t), 138.3 (t), 137.9 (t), 137.6 (t), 134.1 (t), 133.4 (t), 133.2 (q), 133.0 (t), 132.4 (q), 132.3 (t), 132.3 (t), 131.0 (t), 130.7 (t), 129.2 (t), 127.1 (q), 126.9 (q), 126.6 (t), 125.7 (t), 122.9 (t), 83.9 (≡C), 83.4 (≡C), 82.5 (≡C), 82.3 (≡C), 26.3 (CH₂), 24.0 (Me) and 23.1 (Me) (Found: C, 86.8; H, 6.1. C₃₃H₂₈O₂ requires C, 86.8; H, 6.2%).

1,6-Bis(7-oxoocta-1,3,5-trienyl)cyclohepta-1,3,5-triene **20**.—Aq. sodium hydroxide (11 cm³) was added dropwise during 1 h to a stirred solution of the dialdehyde **14** (0.55 g, 2.08 mmol) in acetone (25 cm³) at 3 °C. After being stirred for a further 1 h at 3 °C, the mixture was worked up as for the isolation of compound **16**. The product was chromatographed on alumina (3.2 × 6.2 cm). The fractions eluted with ether-benzene (1:1) afforded the diketone **20** (550 mg, 76%) as red plates, m.p. 167–168 °C (from hexane-benzene); *m/z* 332 (M⁺, 100%) (Found: M, 332.4); λ_{\max}/nm 241 (ϵ 25 500), 348 (109 000) and 443 (16 100); $\nu_{\max}/\text{cm}^{-1}$ 1670 (C=O), 1600 (C=C), 1010 and 980 (E-HC=CH); δ_{H} (500 MHz) 7.20 (2 H, dd, *J* 15.5 and 11.2, H^B), 6.75–6.66 (4 H, m, H^D and H^E), 6.65 (2 H, m, H²), 6.57 (2 H, d, *J* 14.4, H^F), 6.46 (2 H, dd, *J* 13.8 and 11.2, H^C), 6.41 (2 H, m, H¹), 6.31 (2 H, d, *J* 15.5, H^A), 2.73 (2 H, s, CH₂) and 2.29 (6 H, s, Me) (Found: C, 83.3; H, 7.2. C₂₃H₂₄O₂ requires C, 83.1; H, 7.3%).

1,6-Bis(11-methyl-7-oxotrideca-1,3,5,8,10-pentaen-12-ynyl)cyclohepta-1,3,5-triene **27**.—A mixture of ethanolic sodium ethoxide (2.0 cm³) in dry benzene (4.0 cm³) was added dropwise to a solution of the diketone **20** (560 mg, 1.72 mmol) and the aldehyde **21** (1.30 g, 13.8 mmol) in dry benzene (80 cm³) at 7 °C. After being stirred for 1 h at 7 °C, the mixture was worked up as for the isolation of compound **22**. The product was chromatographed on silica gel (3.8 × 11 cm). The fractions eluted with benzene-dichloromethane (1:4) afforded the acyclic diketone **27** (438 mg, 53%) as dark red plates, m.p. 108–110 °C (decomp.) (from hexane-dichloromethane); *m/z* 485 (M⁺ + 1) (FAB method) (Found: M, 484.6); λ_{\max}/nm 299sh (ϵ 40 000), 485 (98 900) and 458 (22 700); $\nu_{\max}/\text{cm}^{-1}$ 3250 (C≡CH), 2100 (C≡C), 1650 (C=O), 1605 (C=C) and 1005 (E-HC=CH); δ_{H} (500 MHz) 7.70 (2 H, dd, *J* 15.4 and 11.4, H^B), 7.37 (2 H, dd, *J* 14.8 and 11.6, H^E), 6.75 (2 H, dd, *J* 14.4 and 10.7, H^G), 6.69 (2 H,

dd, J 14.9 and 10.7, H^H), 6.65 (2 H, m, H^2), 6.57 (2 H, d, J 14.9, H^1), 6.52 (2 H, d, J 14.8, H^D), 6.52 (2 H, m, H^F), 6.46 (2 H, d, J 11.4, H^A), 6.43 (2 H, d, J 15.4, H^C), 6.41 (2 H, m, H^1), 3.51 (2 H, s, $C\equiv CH$), 2.74 (2 H, s, CH_2) and 2.04 (6 H, s, Me) (Found: C, 86.8; H, 6.8. $C_{35}H_{32}O_2$ requires C, 86.7; H, 6.7%).

18,19,20,21-Tetrahydro-17,22-dimethyl-1,6-methano[32]-annulene-13,26-dione **9**.—A solution of compound **27** (380 mg, 0.788 mmol) in pyridine–ether (3:1; 600 cm^3) was added dropwise during 6 h to a stirred solution of anhydrous copper(II) acetate (7.50 g) in pyridine–ether (3:1; 480 cm^3) at 50 °C. After being stirred for a further 30 min at 50 °C, the mixture was worked up as for the isolation of compound **4**. The product was chromatographed on Daiso gel (3.2 × 10.0 cm). The fractions eluted with benzene–dichloromethane (1:4) afforded the tetrahydro[32]annulenedione **9** (120 mg, 32%) as dark purple needles, m.p. 228–230 °C (decomp.) (from hexane–dichloromethane); m/z 482 (M^+ , 32%) and 165 (100) (Found: M , 482.5); for UV data see Table 3; ν_{max}/cm^{-1} 2170 ($C\equiv C$), 1660 ($C=O$), 1010 and 990 ($E-HC=CH$); δ_H (500 MHz) 7.53 (2 H, d, J 14.5 and 11.6, H^E), 7.24 (2 H, dd, J 16.0 and 11.2, H^B), 6.85 (2 H, dd, J 14.5 and 10.4, H^G), 6.79 (2 H, d, J 14.5, H^D), 6.69 (2 H, m, H^2), 6.68 (2 H, d, J 15.2, H^1), 6.61 (2 H, dd, J 15.2 and 10.4, H^H), 6.53 (2 H, d, J 11.2, H^A), 6.51 (2 H, dd, J 14.5 and 11.6, H^F), 6.45 (2 H, m, H^1), 6.31 (2 H, d, J 16.0, H^C), 2.66 (2 H, s, CH_2) and 2.18 (6 H, s, Me); δ_C (125 MHz) 189.6 ($C=O$), 143.8 (t), 143.2 (t), 139.1 (t), 137.3 (t), 137.1 (t), 135.4 (t), 131.8 (q), 131.4 (t), 130.9 (t), 130.9 (t), 127.8 (t), 126.0 (q), 122.9 (t), 84.7 ($\equiv C$), 82.8 ($\equiv C$), 26.5 (CH_2) and 24.9 (Me) (Found: C, 87.0; H, 6.0. $C_{35}H_{30}O_2$ requires C, 87.1; H, 6.3%).

Total Lineshape Analysis of Compound 4.—The lineshapes of the methylene proton signals measured at six temperatures in the range of 0–60 °C in $CDCl_3$ and 26–70 °C in CF_3CO_2D were simulated using the DNMR3 program¹⁷ and the best-fit rate constants were determined for each temperature. Dependence of the chemical-shift difference and T_2 on the temperature were properly taken into account. Least-squares analysis of the Eyring plots afforded the kinetic parameters shown in Table 2.

Saturation Transfer Experiments of Compound 4 in D_2SO_4 .—Dependence of the intensity of the signal at δ 3.89, due to one of the methylene protons, upon the duration of irradiation at the other methylene proton at δ 2.38 was measured. In the case of saturation transfer between strongly coupled protons, the effect of cross-relaxation should be taken into account.^{18b} The experiment was done at a single temperature of 26 °C, to afford a value for the rate constant of 3.3 s^{-1} for exchange of the methylene protons. Observation of the δ 2.38 signal upon irradiation of the δ 3.89 signal gave the same rate constant within experimental error.

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